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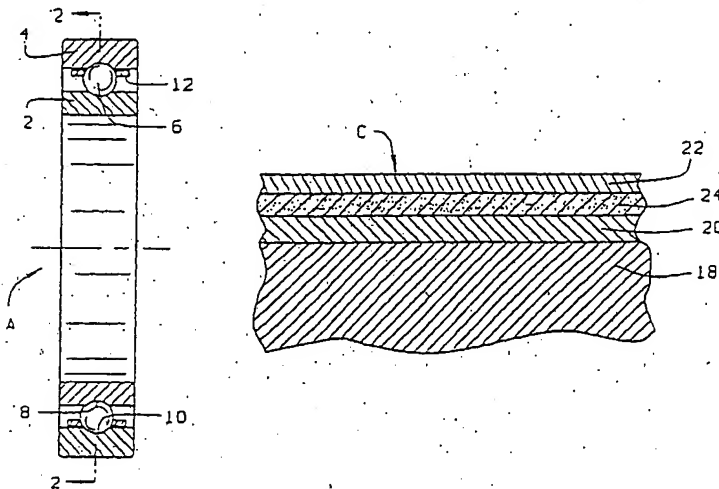
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- (71) Applicant: THE TIMKEN COMPANY [US/US]; 1835
Dueber Avenue, S.W., North Canton, OH 44706-0930
(US).
- (72) Inventors: DRORY, Michael, D.; RFD 2, Box 112, Peter-
borough, NH 03458 (US). DOLL, Gary, L.; 6516 Pebble
Creek Avenue, Canton, OH 44718 (US).
- (74) Agent: BOESCHENSTEIN, Edward, A.; Polster,
Lieder, Woodruff & Lucchesi, L.C., 763 South New Ballas
Road, St. Louis, MO 63141 (US).
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(54) Title: ANTI-FRICTION BEARING FOR USE IN A CORROSIVE ENVIRONMENT



(57) Abstract: An anti-friction bearing (A) that operates in an environment rendered corrosive by a halogen gas or a hydrohalogen acid has races (2 and 4) that are formed from stainless steel and rolling elements (6) that roll along opposed raceways (8 and 10) on the races (2 and 4). The stainless steel of the races (2 and 4) constitutes a substrate (18) over which a coating (C) extends, and that coating contains amorphous carbon in the form of diamond-like carbon (DLC) which is hard and firmly bonded, so that it does not flake, and also carbides to better resist wear. The coating (C) may also contain hydrocarbons. Indeed, the amorphous carbon and hydrocarbons form a matrix in which the carbides are embedded.

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Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

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Antifriction Bearing For Use In A Corrosive EnvironmentTechnical Field

5 This invention relates in general to antifriction bearings for use in corrosive environments, and more particularly to an antifriction bearing of that type which has a carbon-based coating on its critical surface areas.

Some devices rotate at high velocities within environments that are rendered corrosive by halogen gases. In order to sustain high velocities, these devices must be supported on antifriction bearings. Typical of such devices are
10 the rotors within excimer lasers. Also equipment used in the semiconductor processing industry utilizes bearings which operate in environments rich in halogens.

The typical antifriction bearing for accommodating rotation in a corrosive environment has races formed from stainless steel or a ceramic, such
15 as silicon nitride, and rolling elements that are likewise formed from stainless steel or a ceramic. Low and medium steels, from which conventional bearings are formed, react too readily with halogens to serve any useful purpose for bearings that are subjected to halogens. Such bearings deteriorate much too rapidly.

20 Even bearings formed from stainless steel do not resist attack by the more reactive halogen gases, particularly fluorine. Indeed, halogen gases have an affinity for carbides, particularly the carbides of iron and chromium, and when exposed to stainless steel, deplete the steel of those carbides at its surface areas. The steel of the bearing degrades along its surfaces, and at the raceways
25 tend to spall with the movement of the rolling elements over those raceways. Halogen gases, particularly fluorine, also attack ceramics, so races and balls formed from silicon nitride also suffer deterioration, but not as readily but ceramics are otherwise not as well-suited for bearings as is stainless steel.

Antifriction bearings function best when a lubricant film covers their
30 critical surface areas, and in a ball bearing this includes the raceways of the races and the surfaces of the balls. But traditional greases and halogens are not particularly compatible, for the grease breaks down when churned by the balls

in the presence of halogens. To be sure, specialized greases exist for use in bearings that operate in corrosive environments, but even these greases deteriorate in the presence of fluorine.

Most devices having rotors that operate in the presence of halogens have enclosures which isolate their rotors and confine the halogens. Access to a rotor and to the bearings which support it is difficult and requires disassembly of nearby components. Bearing replacement consumes considerable time and requires skilled technicians. As a consequence it is quite costly. Even applying additional grease to the bearings is costly.

Background Art

The present invention resides in an antifriction bearing that operates in an environment rendered corrosive by a halogen gas or a hydrohalogen acid. The bearing includes races and rolling elements located between the races. Each race is formed from stainless steel which provides a substrate for a carbon-based coating. The halogen reduces the surface friction of the coating.

Brief Description of Drawings

Fig. 1 is sectional view of an antifriction bearing provided with a coating in accordance with the present invention:

Fig. 2 is sectional view of the bearing taken along line 2-2 of Fig. 1; and

Fig. 3 is sectional view of the coating.

Best Mode for Carrying Out the Invention

Referring to the drawings, an antifriction bearing A (Figs. 1 and 2) has the capacity to operate for extended periods in an environment rendered corrosive by a halogen gas or a hydrohalogen acid. The bearing A along its critical surfaces has a carbon-based coating C (Fig. 3) which, while being amorphous, is extremely hard and firmly bonded so that, in contrast to graphite, it resists flaking or scaling. Halogens, particularly fluorine, alter the surface energy of the coating such that its coefficient of friction with respect to most other material, particularly those used in bearings, is reduced. In short, the bearing A has low friction surfaces.

The bearing A includes (Figs. 1 and 2) an inner race 2, an outer race 4 which surrounds the inner race 2, yet is spaced from it, and rolling elements in

the form of balls 6 located in the annular space between the races 2 and 4. Actually, the balls 6 contact the inner race 2 along a raceway 8 on the race 2 and contact the outer race 4 along a raceway 10 on the race 4. The two raceways 8 and 10, which are the critical surfaces for the races 2 and 4, take the form of grooves that are concave in cross section, with the curvature generally conforming to the curvature of the balls 6. In addition, the bearing A includes a cage 12 having pockets which receive the balls 6. The cage 12 maintains the proper spacing between the balls 6.

The two races 2 and 4 are formed from a substance, such as stainless steel, that is at least somewhat resistant to attack by halogen gases and hydrohalogen acids. 440C steel represents a suitable stainless steel. The stainless steel of the races 2 and 4 is hardened, at least along the raceways 8 and 10, and that may be achieved by through hardening, induction hardening, or case-carburizing. The balls 6 may likewise be formed from stainless steel, such as 440C steel, that is covered with the coating C or from a ceramic, such as silicon nitride. The cage 14 may also be formed from stainless steel that is covered with the coating C, or it may be formed from a substance of lesser strength which better resists attack by the particular halogen.

Several of the halogen gases and hydrohalogen acids will attack stainless steel, reacting primarily with carbides of chromium and iron in the steel, particularly at the grain boundaries. This produces voids in the steel, so the steel tends to degrade and lose integrity. Actually the degradation is not too significant as to most surface areas on the races 2 and 4, but if it occurs at the raceways 8 and 10, it will adversely affect the operation of the bearing A. After all, the balls 6 roll along the races 2 and 4 at their respective raceways 8 and 10, producing cyclic stresses. If the steel along either raceways 8 or 10 were to degrade, it would spall and transform the otherwise smooth raceways 8 or 10 into a rough surface.

Preferably the carbon-based coating C extends over the entire surface areas of each of the races 2 and 4 and certainly over the raceways 8 and 10. The coating C serves to protect the races 2 and 4 from the deleterious effects of the halogen gas or hydrohalogen acid. Apart from that, the halogen reacts with the

coating C to form a halogenated surface – one that has a more favorable surface energy in the sense that friction along it is reduced. Indeed, the coating C itself serves as a lubricant, eliminating the need for grease or at least reducing the amount of grease required and rendering the depletion of grease less than a catastrophic event.

The stainless steel of each races 2 and 4 forms a substrate 18 to which the carbon-based coating C is bonded. The coating C may include an amorphous carbon known as diamond like carbon (DLC). In this form the coating C is actually stratified. It includes (Fig. 3) a metallic base layer 20 that is against the stainless steel substrate 18, a surface layer 22 that is exposed to the halogen gas or hydrohalogen acid, and an intervening layer 24 between the metallic base layer 20 and the surface layer 22. The thickness of coating C ranges between 0.1 μm (micrometers) and 2.0 μm and is preferably about 1.0 μm . While well-defined boundaries or interfaces do not exist between the layers 20, 22 and 24, inasmuch as adjacent layers blend, the base layer 20 is about 10% of the thickness of the coating C, the surface layer 22 between about 70% and 80%, and the intervening layer 24 between about 10% and 20%.

The base layer 20 consists of a metal that bonds well and easily to the stainless steel substrate 18 and bonds with carbon and hydrocarbons as well. Suitable metals for the layer 20 include chromium, molybdenum, tungsten and titanium. Whatever the metal, it is applied to the stainless steel substrate 18 preferably by physical vapor deposition. To this end, the substrate 18 is thoroughly cleaned, preferably by sputtering. Then the metal desired for the base layer 20 is introduced into a plasma of inert gas and deposited on the substrate 18 by physical vapor deposition, with the substrate 18 being maintained at a relatively low temperature on the order of 300° F or less. The metal which is deposited diffuses into the substrate 18, establishing a firm bond, and builds up on itself to form the base layer 20.

The intervening layer 24 contains the same metal as the base layer 20 and in addition contains carbon and hydrocarbons. It too is deposited by vapor deposition – a combination of physical vapor deposition and chemical vapor deposition. Both the metal and a hydrocarbon, such as methane, ethylene, or

acetylene, are introduced into an inert gas plasma which impinges on the base layer 20, depositing the metal along with carbon and hydrocarbons. The hydrocarbon which enters the plasma disassociates and some of the carbon and hydrogen recombines so that the hydrocarbon which is deposited on the base layer 20 is not necessarily the same as the basic hydrocarbon that is introduced into the plasma. As the intervening layer 24 grows, the content of metal is decreased and the content of carbon and hydrocarbons is increased.

Where the intervening layer 24 blends into the base layer 20, the composition of the intervening layer 24 is primarily metal, whereas the intervening layer 24 blends into the surface layer 22, the intervening layer 24 is primarily carbon and hydrocarbon.

The surface layer 22 consists primarily of carbon and hydrocarbon, but it does have carbides within it. It is derived by chemical vapor deposition. To this end an inert gas plasma is directed at the intervening layer 24. A gaseous hydrocarbon such as methane, ethylene, or acetylene is introduced into the plasma along with minute particles of a metal which will readily unite with carbon to form a hard carbide that is somewhat resistant to attack by halogens. Suitable metals for the particles are tungsten, molybdeum and titanium. The size of the particles should be somewhat less than the thickness of the surface layer 22.

The plasma transforms the metal hydrocarbon into carbon and different hydrocarbons and some of the carbon unites with the metal of the particles to form hard carbide particles. The carbons and hydrocarbons produce a somewhat elastic matrix in which the hard carbide particles are embedded.

Preferably the balls 6 are also formed from stainless steel with the same coating C over the stainless steel. The low friction surfaces formed by the coatings C on the raceways 8 and 10 and the coatings C on the balls 6, when in the presence of a halogen such as fluorine, produces a well-lubricated bearing A, even in the absence of traditional forms of lubrication. On the other hand, the balls 6 may be formed from silicon nitride, even though at least fluorine will attack it, although somewhat slowly.

The cage 12 likewise may be formed from stainless steel that is covered with the coating C. However, the cage 12 does not see the stresses to which the races 2 and 4 and the balls 4 are subjected, and may be formed from different materials as long as the material is capable of resisting corrosion in the presence of halogens. Teflon, which is available from E.I. duPont, is one material suitable for the cage 12.

In the operation of the bearing A, the somewhat elastic matrix holds the carbide particles in place over the stainless steel substrate 18. The carbide particles in turn resist wear. But the matrix, formed from carbon and hydrocarbons does more than hold the particles in place. It further protects the stainless steel, and the carbides as well, from the reactive halogens – which is particularly important insofar as fluorine and hydrofluoric acid are concerned. Moreover, the hydrocarbon reacts with halogens, chemically or otherwise, to alter the surface energy of the coating C such that the coefficient of friction between the coating C and that which moves over it, usually the balls 6, is reduced. In other words, in the presence of a halogen, the coating C provides a low friction surface.

The carbon-based coating C remains intact until it is eventually worn away, and while it does wear away, the bonds within it remain strong, and it does not flake or scale as would graphite. Moreover, the coating C lasts considerably longer than the special greases which are designed to operate in corrosive environments. Indeed, should the bearing A contain such a grease, it will operate satisfactorily when the grease dissipates. In the absence of grease, the bearing A relies on the low coefficient of friction between the balls 6 and the coating C along the raceways 8 and 10 to maintain friction at acceptable levels within the bearing A.

In lieu of having a carbon-hydrocarbon constituency, the matrix of the surface layer 22 and intervening layer 24 may contain simply amorphous carbon – albeit diamond-like carbon.

In lieu of diamond-like carbon together with hydrocarbons and metal carbides, the coating C may take the form of synthetic diamonds. A synthetic

diamond coating C will at low temperature resist corrosion in the presence of halogens, yet will react with the halogens to produce a low friction surface.

The coating C may be applied to races and rolling elements of bearings other than ball bearings, tapered roller bearings, cylindrical roller bearings and
5 spherical roller bearings to name several.

Claims:

1. In combination with an environment rendered corrosive by the presence of a halogen gas or a hydrohalogen acid, an antifriction bearing comprising: a first race having a raceway; a second race having a raceway presented opposite, yet spaced from, the raceway of the first race; and rolling elements located between raceways of the two races, such that when the first race rotates relative to the second race the rolling elements will roll along the raceways, at least one of the races having a coating along its raceway, with the coating comprising a substantial proportion of amorphous carbon.
2. The combination according to Claim 1 wherein the coating contains diamond-like carbon.
3. The combination according to Claim 1 wherein the races are formed from stainless steel.
4. The combination according to Claim 3 wherein the coating is on each race at its raceway, and the stainless steel forms a substrate on the race.
5. The combination according to Claim 4 wherein the coating comprises a metal base layer bonded to the substrate of the race on which the coating is located, a carbon-based surface layer exposed to and in contact with the rolling elements, and an intervening layer which contains both metal and carbon, but proportionally less metal than the base layer and less carbon than the surface layer.
6. The combination according to Claim 5 wherein the surface layer contains amorphous carbon and hydrocarbons and also carbides.
7. The combination according to Claim 6 wherein the base layer is selected from a group consisting of chromium, tungsten, molybdenum, and titanium.
8. The combination according to Claim 1 wherein the atmosphere is rich in fluorine.
9. The combination according to Claim 1 wherein the coating extends along each race at its raceway.

10. The combination according to Claim 9 wherein each rolling element includes a stainless steel substrate and a carbon-based coating over that substrate.

5 11. In combination with an environment that is rich in fluorine, an antifriction bearing comprising: a first race providing a substrate formed from stainless steel and having a raceway and a carbon-based coating over the substrate at the raceway; a second race providing a substrate formed from stainless steel and having a raceway and a carbon-based coating over the substrate at that raceway, the raceway on the second race being presented
10 toward the raceway on the first race, and rolling elements located between the races at their raceways and bearing against the coatings at the raceways, such that when one race rotates relative to the other race the rolling elements roll along the coatings at the raceways.

12. The combination according to Claim 11 wherein the coating
15 along its exposed surface includes an amorphous carbon and carbides embedded in the amorphous carbon.

13. The combination according to Claim 12 wherein the coating also includes hydrocarbons.

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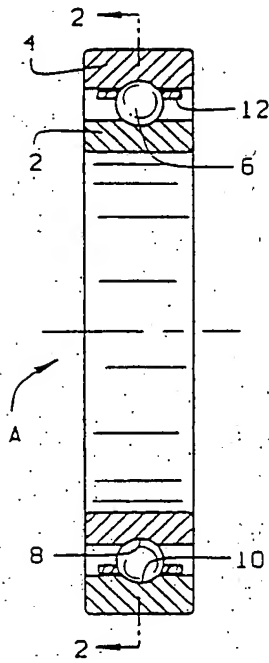


FIG. 1

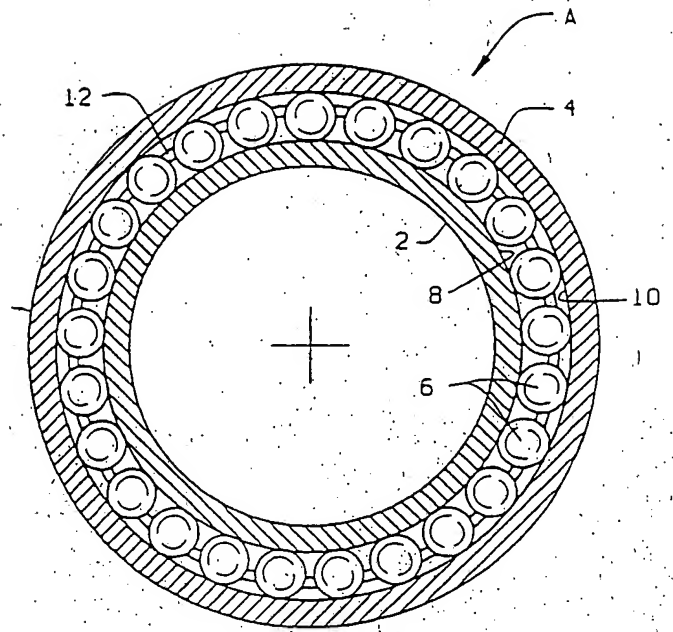


FIG. 2

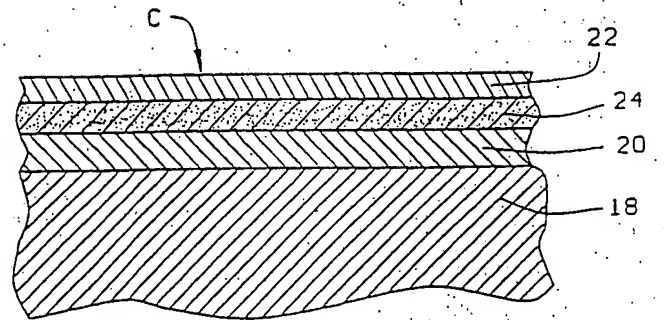


FIG. 3

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 F16C33/62 F16C33/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 F16C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 548 (M-1689), 19 October 1994 (1994-10-19) & JP 06 193637 A (NTN CORP), 15 July 1994 (1994-07-15) abstract	1,2,9
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 03, 28 April 1995 (1995-04-28) & JP 06 341445 A (KOYO SEIKO CO LTD), 13 December 1994 (1994-12-13) abstract	1,2,11

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

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Baron, C

INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 14512 A (SKF IND TRADING & DEV) 25 March 1999 (1999-03-25) page 2; line 4 - line 32 page 3; line 29 - line 33; figures 1, 2	1-4, 9-12
A	---	6, 7
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 08, 29 August 1997 (1997-08-29) & JP 09 094911 A (NTN CORP), 8 April 1997 (1997-04-08) abstract	1-4, 10, 11
P, X	---	
P, X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 08, 6 October 2000 (2000-10-06) & JP 2000 136828 A (KOYO SEIKO CO. LTD), 16 May 2000 (2000-05-16) abstract	1, 2, 9, 11
P, X	---	
P, X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 05, 14 September 2000 (2000-09-14) & JP 2000 049140 A (SPEEDFAM-IPEC CO LTD), 18 February 2000 (2000-02-18) abstract	1-3, 11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/29671

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 06193637 A	15-07-1994	NONE	
JP 06341445 A	13-12-1994	JP 2991834 B	20-12-1999
WO 9914512 A	25-03-1999	NL 1007046 C	17-03-1999
		CN 1269875 T	11-10-2000
		EP 1015780 A	05-07-2000
JP 09094911 A	08-04-1997	NONE	
JP 2000136828 A	16-05-2000	NONE	
JP 2000049140 A	18-02-2000	NONE	

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